

09/719731

Practitioner's Docket No. R00099US (#90568)

CHAPTER II

Preliminary Classification:

Proposed Class: 524

Subclass: 701

NOTE: "All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P., § 601, 7th ed.

TRANSMITTAL LETTER
TO THE UNITED STATES ELECTED OFFICE (EO/US)

(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/01246	26 FEBRUARY 1999	14 MARCH 1998
TITLE OF INVENTION		
SILICONE CONTACT ADHESIVE WITH REDUCED COLD FLOW		
APPLICANT(S)		
SCHMITZ, Christoph and BRACHT, Stefan		

Box PCT

Assistant Commissioner for Patents

Washington D.C. 20231

ATTENTION: EO/US

CERTIFICATION UNDER 37 C.F.R. § 1.10*

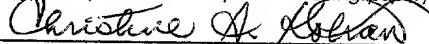
(Express Mail label number is mandatory.)

(Express Mail certification is optional.)

I hereby certify that this Transmittal Letter and the papers indicated as being transmitted therewith is being deposited with the United States Postal Service on this date DECEMBER 15, 2000, in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EK980729387US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

CHRISTINE A. KOTRAN

(type or print name of person mailing paper)



Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. § 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

***WARNING:** Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. § 1.10(b).
"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

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NOTE: To avoid abandonment of the application, the applicant shall furnish to the USPTO, not later than 20 months from the priority date: (1) a copy of the international application, unless it has been previously communicated by the International Bureau or unless it was originally filed in the USPTO; and (2) the basic national fee (see 37 C.F.R. § 1.492(a)). The 30-month time limit may not be extended. 37 C.F.R. § 1.495.

WARNING: Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail procedure of 37 C.F.R. § 1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing—See 37 C.F.R. § 1.8.

NOTE: Documents and fees must be clearly identified as a submission to enter the national state under 35 U.S.C. § 371 otherwise the submission will be considered as being made under 35 U.S.C. § 111. 37 C.F.R. § 1.494(f).

I. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. § 371:

- a. ☐ This express request to immediately begin national examination procedures (35 U.S.C. § 371(f)).
- b. ☒ The U.S. National Fee (35 U.S.C. § 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

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2. Fees

CLAIMS FEE	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
XXXX	TOTAL CLAIMS	11 - 20 =	---	× \$18.00 =	\$ ---
	INDEPENDENT CLAIMS	1 - 3 =	---	× \$78.00 =	---
	MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$260.00				---
	BASIC FEE** <input type="checkbox"/> U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an international preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO: <input type="checkbox"/> and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(1) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 C.F.R. § 1.492(a)(4)) \$96.00 <input type="checkbox"/> and the above requirements are not met (37 C.F.R. § 1.492(a)(1)) \$670.00				
XXXX	U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO: <input type="checkbox"/> has been paid (37 C.F.R. § 1.492(a)(2)) \$690.00 <input type="checkbox"/> has not been paid (37 C.F.R. § 1.492(a)(3)) \$970.00 where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 C.F.R. § 1.492(a)(5)) \$860.00				
	Total of above Calculations = 860.00				
	Reduction by 1/2 for filing by small entity, if applicable. Affidavit must be filed also. (note 37 C.F.R. § 1.9, 1.27, 1.28)				
	Subtotal 860.00				
	Total National Fee \$ 860.00				
	Fee for recording the enclosed assignment document \$40.00 (37 C.F.R. § 1.21(h)). (See Item 13 below). See attached "ASSIGNMENT COVER SHEET".				
TOTAL	Total Fees enclosed				\$ 860.00

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*See attached Preliminary Amendment Reducing the Number of Claims.

- i. ~~XXXX~~A check in the amount of \$860.00 to cover the above fees is enclosed.
- ii. ☐ Please charge Account No. _____ in the amount of \$ _____.
A duplicate copy of this sheet is enclosed.

****WARNING:** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date: * * * (2) the basic national fee (see § 1.492(a)). The 30-month time limit may not be extended." 37 C.F.R. § 1.495(b).

WARNING: If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office. 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

3. ☒ A copy of the International application as filed (35 U.S.C. § 371(c)(2)):

NOTE: Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment. "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☒ is transmitted herewith.
- b. ☐ is not required, as the application was filed with the United States Receiving Office.
- c. ☐ has been transmitted
- i. ☐ by the International Bureau.
Date of mailing of the application (from form PCT/1B/308): _____
- ii. ☐ by applicant on _____
Date

4. ☒ A translation of the International application into the English language (35 U.S.C. § 371(c)(2)):

- a. ☒ is transmitted herewith.
- b. ☐ is not required as the application was filed in English.
- c. ☐ was previously transmitted by applicant on _____
Date
- d. ☐ will follow.

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5. ☒ Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. § 371(c)(3)):

NOTE: The Notice of January 7, 1993 points out that 37 C.F.R. § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that: "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1.121. In many cases, filing an amendment under section 1.121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O.G. 29-40, at 36.

- a. ☐ are transmitted herewith.
- b. ☐ have been transmitted
- i. ☐ by the International Bureau.
Date of mailing of the amendment (from form PCT/1B/308): _____
- ii. ☐ by applicant on (date) _____
Date

- c. ☒ have not been transmitted as

- i. ☒ applicant chose not to make amendments under PCT Article 19.
Date of mailing of Search Report (from form PCT/ISA/210.): 03 AUGUST 1999
- ii. ☐ the time limit for the submission of amendments has not yet expired.
The amendments or a statement that amendments have not been made will be transmitted before the expiration of the time limit under PCT Rule 46.1.

6. ☐ A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. § 371(c)(3)):
- a. ☐ is transmitted herewith.
- b. ☐ is not required as the amendments were made in the English language.
- c. ☐ has not been transmitted for reasons indicated at point 5(c) above.
7. ☒ A copy of the international examination report (PCT/IPEA/409)
- ☒ is transmitted herewith. (NO ANNEXES.)
- ☐ is not required as the application was filed with the United States Receiving Office.
8. ☐ Annex(es) to the international preliminary examination report
- a. ☐ is/are transmitted herewith.
- b. ☐ is/are not required as the application was filed with the United States Receiving Office.
9. ☐ A translation of the annexes to the international preliminary examination report
- a. ☐ is transmitted herewith.
- b. ☐ is not required as the annexes are in the English language.

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10. ☒ An oath or declaration of the inventor (35 U.S.C. § 371(c)(4)) complying with 35 U.S.C. § 115

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- a. ☐ was previously submitted by applicant on _____
Date
- b. ☐ is submitted herewith, and such oath or declaration
- i. ☐ is attached to the application.
- ii. ☐ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. § 1.70.
- c. ☒ will follow.

II. Other document(s) or information included:

11. ☒ An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a):
- a. ☒ is transmitted herewith.
- b. ☐ has been transmitted by the International Bureau.
Date of mailing (from form PCT/IB/308): _____
- c. ☐ is not required, as the application was searched by the United States International Searching Authority.
- d. ☐ will be transmitted promptly upon request.
- e. ☐ has been submitted by applicant on _____
Date
12. ☒ An Information Disclosure Statement under 37 C.F.R. §§ 1.97 and 1.98:
- a. ☐ is transmitted herewith.
Also transmitted herewith is/are:
- ☐ Form PTO-1449 (PTO/SB/08A and 08B).
- ☐ Copies of citations listed.
- b. ☒ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. § 371(c).
- c. ☐ was previously submitted by applicant on _____
Date
13. ☐ An assignment document is transmitted herewith for recording.
A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

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14. ☒ Additional documents:
- ☐ Copy of request (PCT/RO/101)
 - ☒ International Publication No. W0 99/47619
 - ☐ Specification, claims and drawing
 - ☒ Front page only
 - ☒ Preliminary amendment (37 C.F.R. § 1.121)
 - ☒ Other PETITION FOR REVIVAL OF AN INTERNATIONAL APPLICATION FOR PATENT...UNDER 37 CFR 1.137(b); TERMINAL DISCLAIMER; NOTIFICATION OF RECORDING OF A CHANGE; WRITTEN OPINION AND RESPONSE THERETO;
PCT/IPEA/416 / Petition & Disclaimer fees
15. ☒ The above checked items are being transmitted
- ☐ before 30 months from any claimed priority date.
 - ☒ after 30 months.
16. ☐ Certain requirements under 35 U.S.C. § 371 were previously submitted by the applicant on _____, namely:
- _____
- _____
- _____
- _____

AUTHORIZATION TO CHARGE ADDITIONAL FEES

WARNING: Accurately count claims, especially multiple dependant claims, to avoid unexpected high charges if extra claims are authorized.

NOTE: "A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).

NOTE: "Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).

☒ The Commissioner is hereby authorized to charge the following additional fees that may be required by this paper and during the entire pendency of this application to Account No. 08-2441

☒ 37 C.F.R. § 1.492(a)(1), (2), (3), and (4) (filing fees)

WARNING: Because failure to pay the national fee within 30 months without extension (37 C.F.R. § 1.495(b)(2)) results in abandonment of the application, it would be best to always check the above box.

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☒ 37 C.F.R. § 1.492(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.

☒ 37 C.F.R. § 1.17 (application processing fees)

☒ 37 C.F.R. § 1.17(a)(1)-(5) (extension fees pursuant to § 1.136(a).

☐ 37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. § 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying . . . issue fee." From the wording of 37 C.F.R. § 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

☐ 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).



SIGNATURE OF PRACTITIONER

D. PETER HOCHBERG

(type or print name of practitioner)

D. PETER HOCHBERG CO., L.P.A.

P.O. Address

1940 E. 6TH STREET - 6TH FLOOR

CLEVELAND, OH 44114-2294

Reg. No.: 24,603

Tel. No.: (216) 771-3800

Customer No.:

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Christoph Schmitz and Stefan Bracht

Serial No.:

Filed: (Herewith)

Title: SILICONE CONTACT ADHESIVE WITH REDUCED COLD FLOW

Attorney File: RO0099US (#90568)

Box PCT
Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Prior to the substantive examination of the above-identified application, please amend the application without prejudice as follows:

In the claims:

Claim 1, line 5, delete "characterized in that" and insert -- wherein --.

Claim 2, line 1, delete "characterized in that" and insert -- wherein --.

Claim 3, line 1, delete "characterized in that" and insert -- wherein --.

4. (Amended) Process according to [one or more of the preceding claims, characterized in that] claim 1, wherein the organic complex former is substantially removed during drying.

5. (Amended) Process according to [one or more of the preceding claims, characterized in that] claim 1, wherein the drying is carried out at a temperature of between 20 and 120°C.

6. (Amended) Process according to [one or more of the preceding claims, characterized in that] claim 1, wherein the weight per unit area of the dried film is between 10 and 300 g/m².

7. (Amended) Process according to [one or more of the preceding claims, characterized in that] claim 1, wherein the organic complex former is acetylacetone or that acetylacetone participates in the complex forming.

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8. (Amended) Process according to [one or more of the preceding claims characterized in that] claim 1, wherein the metal participating in the complex is one of aluminum [or] and titanium.

9. (Amended) Process according to [one or more of the preceding claims, characterized in that] claim 1, wherein the polysiloxane is substantially polydimethyl siloxane.

10. (Amended) Process according to claim 9, [characterized in that] wherein the free silanol groups present in the polydimethyl siloxane are chemically deactivated through a suitable endcapping and are [thus] amine-resistant.

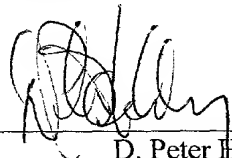
11. (Amended) Medicinal patch[, characterized in that in its] having a layered structure, said structure having [it has] at least one layer of a polysiloxane pressure-sensitive adhesive produced by means of a process [according to one of the preceding claims] defined in claim 1.

REMARKS

The foregoing amendments to the claims are made to delete multiple-dependencies therein, thus reducing the government filing fee, and to place them in conformance with U.S. patent practice. Accordingly, prosecution on the merits hereof is respectfully requested.

Respectfully submitted,

By: _____



D. Peter Hochberg
Reg. No. 24,603

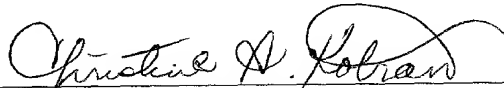
DPH/ck

D. Peter Hochberg Co., L.P.A.
1940 E. 6th Street - 6TH Floor
Cleveland, Ohio 44114-2294
(216) 771-3800

EXPRESS MAIL CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that the foregoing Preliminary Amendment and any document(s) referred to as attached hereto is being deposited with the United States Postal Service on the date noted below in an envelope as "Express Mail Post Office to Addressee" mailing Label Number EK980729387US addressed: Box PCT, Commissioner for Patents, Washington, D.C. 20231

Date: December 15, 2000



Christine A. Kotran

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SILICONE CONTACT ADHESIVE WITH REDUCED COLD FLOW

The invention relates to reagents for cross-linking pressure-sensitive adhesive formulations on the basis of silicone polymers.

Apart from other technical applications, such pressure-sensitive adhesive formulations are mainly employed in the manufacture of medicinal patches. Among the medicinal patches, these silicone pressure-sensitive adhesives which are cross-linked in a novel manner are especially suited for the production of active substance-containing medicinal patches, i.e. of transdermal therapeutic systems (TTS).

The described cross-linking reagents are employed according to the invention in the solvent-containing coating and drying of pressure-sensitive silicone adhesive formulations.

It is only under these conditions that the reagents develop their cross-linking action, which results in the formation of a three-dimensional polymer network.

The resultant pressure-sensitive adhesive layers thereby lose their flowability - their so-called "cold flow".

Cold flow is an undesirable phenomenon because when it occurs, two surfaces bonded to each other by a pressure-sensitive adhesive layer can be displaced relative to each other even under the influence of gravity, so that a position-constant bond between these surfaces cannot be ensured.

In the case of TTS, this problem especially concerns the adhesive bonding of the system to the application site on

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humans or animals. Furthermore, when cold flow sets in within the silicone adhesive layer comprised in the TTS, the influence of gravity and of cohesion and adhesion forces can result in undesirable deformation and shifting within the system even during storage.

It has now surprisingly been found that the cross-linking reagents employed in the cross-linking of polyacrylate-based pressure-sensitive adhesives can also be successfully used with silicone polymers, despite the fact that the chemical properties of said silicone polymers are fundamentally different from those of polyacrylates.

Organometallic complexes of certain metal cations have proved to be especially effective. Among these, complexes of metals such as aluminum, titanium, zirconium or zinc are particularly preferred according to the invention. As an organic complex former, acetylacetone is particularly suited for medical application.

The cross-linking reagents are added to the solution of the silicone pressure-sensitive adhesive and develop their cross-linking action only after the solvents or stabilizing additives have been removed by drying.

Pressure-sensitive adhesives based on silicone polymers are of particular significance in medical application. This is due to their excellent dermatological compatibility with regard to the triggering of skin irritations and immunological reactions (sensibilization, allergization). In addition, silicone pressure-sensitive adhesives are products which adhere to human skin reliably and over a longer period of time, up to several days. Their strongly water-repellent nature also plays a role in this context.

In the TTS field, silicone pressure-sensitive adhesives stand out for their good chemical compatibility with phar-

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maceutical active agents and auxiliary substances, which promotes the chemical stability and storability of products based on said adhesives. The unusually high permeability (diffusibility) of the silicone polymers, which facilitates the release of contained active and auxiliary agents, is also of particular significance.

Besides these advantages, the silicone pressure-sensitive adhesives available on the market for medicinal application (e.g. product line Bio-PSA Q7 by Dow Corning Company) show considerable deficits as regards their rheological properties.

These products are polysiloxane-based polymers exhibiting no three-dimensional cross-linking or only one limited to microscopic areas. They have a structure that is substantially threadlike and branched to only a small extent or not at all.

This is necessary so that the products can be dissolved at all in organic solvents such as e.g. short-chain alkanes (heptane, petrol) or ethyl acetate, and so that they can be subjected to solvent-containing processing.

Furthermore, these prior art polymers are one-component polymer solutions.

One-component means that the polymers contained in the solution are not intended, in their further processing, for a two-component reaction in the known sense of resin and hardener.

One-component does not, however, mean that the solution may not contain more than one type of polyoxisiloxane polymer, optionally also in admixture with chemically different polymers (e.g. polyacrylates).

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The procedures employed in the processing of one-component polysiloxane pressure-sensitive solutions described in the following must not be confused with those procedures and catalysts that have been described in manifold ways for two-component silicone adhesives. Such systems contain at least two different types of polysiloxanes which are intended, during their further processing, for a reaction yielding a three-dimensional polymer network in the sense of resin and hardener.

The term polysiloxane also comprises mixed polymers of polysiloxane to whose polymer chains chemically different sections, for example on the basis of polyethylene oxide, polypropylene oxide, polyvinyl pyrrolidone or poly(meth)acrylate, are incorporated or added.

In the field of TTS production, the processing of polysiloxane pressure-sensitive adhesive solutions comprises spreading and drying to form thin, pressure-sensitive polymer films.

In the processed state, the lack of three-dimensional cross-linking proves a disadvantage, as the threadlike polymer chains retain a certain flowability, even if an extremely slow one. This is referred to as "cold flow" by the experts since it occurs even at room temperature.

The following forces can all promote such a flow:

1. gravity
2. all mechanical forces that may have an effect on the product during production or storage,
3. adhesion forces between the pressure-sensitive polymers and the surfaces they cover (resulting in contraction or spreading)
4. cohesion forces in the polymer itself (contraction).

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Cold flow practically always has disadvantageous effects during the storage of TTS, which may typically be for a period of two years or more. In this way, e.g. conglutination of the products with their packages may result.

The phenomenon also undesirably arises upon application to the human or animal skin, especially promoted by the warm body temperature. When the TTS is worn for several hours or days, the result may be a displacement thereof caused by the TTS practically flowing over the skin. Furthermore, the silicone pressure-sensitive adhesive may spread on the skin by slowly flowing beyond the area originally provided with adhesive. This frequently leads to residue remaining on the skin along the marginal area of the system after removal of the system. This residue is regarded as extremely annoying by the user.

The problem of cold flow in silicone pressure-sensitive adhesives is known. US 5,232,702 describes a large number of possible countermeasures. The document mentions various types of fillers and additives; however, none of these is described as a cross-linking reagent.

In connection with active-substance systems, cross-linking reactions are even expressly described as being problematic or impossible because the required temperatures are too high or because of a lacking biocompatibility of the reagents (column 5, lines 3-10).

A great number of other cohesion-enhancing measures are described instead.

As these measures do not, in practice, always enable the control of the problem, it was the object of the invention to provide novel and more efficient methods for suppressing cold flow in silicone pressure-sensitive adhesives.

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This object is surprisingly achieved by adding reagents which are employed for the suppression of cold flow in a chemically completely different family of pressure-sensitive adhesive polymers, namely polyacrylates.

This transferred applicability was not to be expected since polysiloxanes, as the skeletal structure of silicone polymers, are of a completely different chemical nature than polyacrylates, which are built up of pure hydrocarbon chemistry.

It is known to those skilled in the art that with polyacrylate pressure-sensitive adhesives containing free carboxyl or hydroxyl groups bound to the polymer, it is possible to attain three-dimensional cross-linking of polymer chains by addition of multivalent ions, e.g. of calcium, magnesium or zinc, but especially of aluminum and the elements of the 4th subgroup, titanium, zirconium and hafnium. Aluminum only occurs as a trivalent ion; as regards the elements of the 4th subgroup, the stable oxidation state +4 is employed.

In this way it becomes possible to postpone the conversion of the bed of threadlike polymer chains into a no longer flowable three-dimensional network until the drying from a solution is carried out.

To be able to use the metal ions in mostly organic solvents on the one hand, and on the other hand to prevent a premature cross-linking reaction in the polymer solution, organic, low-molecular complex formers are employed to which the metal ions are initially bound. Among these complex formers, acetylacetone assumes a special role in the field of medicine, as it is of relatively uncritical toxicology and, in addition, can be readily removed from the product in drying processes.

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Acetylacetone is, in its chemical enol form, a vinylogous acid and forms complexes with the metal ions - the corresponding acetylacetonates. These complexes are of their own chemical nature, with particular stability, and cannot be compared to common salts of organic acids with the respective metals.

Aluminum acetylacetonate and titanyl acetylacetonate are used to cross-link polyacrylate pressure-sensitive adhesives during drying from organic solvents.

In the course of the cross-linking, a transfer of the metal ions from the complex former to the functional groups of the acrylate polymer takes place, whereby several functional groups on different polymer chains are cross-linked.

With regard to the cross-linking reagents aluminum acetylacetonate and titanyl acetylacetonate, which are very frequently used with polyacrylates, it has now surprisingly been found that they have a practically identical effect, phenomenologically, when used with polysiloxanes, despite the fact that these have an entirely different chemistry: the flowability of silicone pressure-sensitive adhesives is significantly reduced.

The characteristics of this change in the case of polysiloxanes are so similar to those in the case of polyacrylates that one may assume that a three-dimensional cross-linking takes place - via a mechanism the details of which are not known.

The novel manner of cross-linking was tested on two groups of silicone pressure-sensitive adhesives that are of particular significance for medical application: on pressure-sensitive adhesives on the basis of polydimethyl siloxane, in a non-amine-compatible form on the one hand and on the other hand in an amine-compatible form.

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The non-amine-compatible form is characterized in that a remainder of silanol groups (hydroxyl groups bound to silicon) remains in the polymer upon polymerization. This is the standard type which is capable of undesired reaction with primary, secondary or tertiary amine groups via the silanol groups.

As many pharmaceutical active substances contain amine groups, amine-compatible types are available especially for application in TTS. These are subjected to a so-called end-capping: the silanol groups are deactivated through suitable reagents, e.g. by addition of a trimethylsilyl group.

A pressure-sensitive adhesive on the basis of a polyacrylate with a low proportion of free carboxyl groups was used for comparison. The three-dimensional cross-linkability of such acrylates through the cross-linkers discussed here is commonly known to those skilled in the art.

The following formulations were examined:

cross-linker: Al-acetylacetonate [% Al ³⁺ (w/w)]	---	0.01	0.025	0.05
polyacrylate pressure-sensitive adhesive Durotak 387-2051	A11	A12	A13	A14
silicone pressure-sensitive adhesive Bio-PSA Q7-4602	S31	---	---	S32

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cross-linker: Ti-acetylacetonate [% Ti ⁴⁺ (w/w)]	---	0.05	0.1	0.2
silicone pressure- sensitive adhesive Bio-PSA Q7-4602	S11	S12	S13	S14
silicone pressure- sensitive adhesive Bio-PSA Q7-4301	S21	S22	S23	S24

Al = aluminum; Ti = titanium

The indicated cross-linker concentrations relate to the dried adhesive mass.

Bio-PSA Q7-4602, produced by Dow Corning, is the solution of a non-amine-compatible pressure-sensitive silicone adhesive in ethyl acetate. Product 4301 differs from the above in that it is amine-compatible. The solvent used here is heptane. Durotak 387-2051, produced by National Starch, is the solution of a polyacrylate pressure-sensitive adhesive in a mixture of ethyl acetate and heptane without the addition of a cross-linker.

The adhesive masses were produced by adding the corresponding amount of a 2% solution of titanyl acetylacetonate in ethanol or a 4% solution of aluminum acetylacetonate in ethyl acetate to the adhesive solution and subsequent mixing.

The viscous adhesive solutions were spread in a thin layer onto a polyethylene terephthalate film (Hostaphan RN 100, produced by Hoechst) with the help of a suitable film-stripping frame and dried for 10 minutes at 80°C in an exhaust-air oven. For all formulations, the layer thickness was adjusted so that the resultant weight per unit area of

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the dried film was $60 \text{ g/m}^2 \pm 5\%$. This corresponds to 6 mg/cm^2 and a layer thickness of approximately $60 \text{ }\mu\text{m}$.

With all of the tested pressure-sensitive adhesives, the coating onto polyethylene terephthalate results in a bond that can mechanically barely be dissolved. Alternately, the pressure-sensitive adhesive films were also, under otherwise identical conditions, produced on a carrier film equipped with a non-stick finish through coating with a fluorated polymer (ScotchPak 1022, produced by 3M). Under these conditions, the pressure-sensitive adhesive film can easily be mechanically removed from the carrier film and subjected to further processing.

The effects of the cross-linking additive were examined in the thus produced pressure-sensitive adhesive layers with two measuring methods, pertaining to apparatus:

The tack or tackiness of a pressure-sensitive adhesive describes its ability to spontaneously adhere to a surface.

This spontaneous tackiness, resulting after only an extremely short period of contact without any notable exertion of pressure, depends considerably on the flowability of the pressure-sensitive adhesive. A high flowability enables a rapid establishment of contact, covering the microstructure of a substrate surface in its entirety, and thus results in a high tack. Flowability is not the only characteristic determining the tack, but it is the most important.

The "rolling ball" method is a suitable measuring method for registering the tack. In this method, a ball made of a suitable material is provided with a starting speed and then let roll over the pressure-sensitive adhesive affixed to a planar carrier in a thin layer.

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The distance after which the ball comes to a halt through the braking effect of the pressure-sensitive adhesive, which depends on the tack, can be evaluated, or else the time can be measured that the ball needs to cover a certain distance without coming to a standstill within this distance. The results of this second variation are not distorted by the often erratic course of the ball's "getting stuck".

The run time of the ball was measured on an inclined plane (glass plate with a strength of 1 cm) with an adjustable angle of inclination over a distance of 59 cm. With a defined preliminary distance of 17.5 cm, the ball was let roll onto the pressure-sensitive adhesive film, which was affixed to a polyethylene terephthalate film.

The run time was measured between two modulated infrared light barriers by means of a connected electronic timer with a display of 1/1000 seconds.

At an inclination angle of 35°, using a high-quality steel rolling-element bearing ball with a diameter of 18 mm, the run times shown in Fig. 1 were determined as the median values of 6 measurements each.

For all three types of adhesive, the measurements show a decrease in the run time correlated to the increase of the cross-linker concentration. Thus, the tack of pressure-sensitive silicone adhesives decreases through the addition of cross-linkers in a way as would have been expected, in theory, for a cross-linking and thus reduction of the flowability of the polymer, and as also becomes evident in the known example of the cross-linking of the polyacrylate (A11-A14).

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This especially holds true for the non-amine-compatible silicone adhesive (S11-S14), but definitely also for the amine-compatible variety (S21-S24).

In addition, it becomes evident that the cross-linking is especially effective in the concentration range of up to 0.05% and also between 0.05% and 0.1% of aluminum.

The use of aluminum-based cross-linkers (S31+S32) instead of titanium-based ones (S11+S12) with silicone pressure-sensitive adhesives turns out to equally effective (Fig.2).

In addition, the shear strength of the produced pressure-sensitive adhesive films was tested.

If a shear force is applied to uncross-linked, threadlike, flowable polymers, a slow flowing of the film occurs. As long as the shearing is not too fast and the film does not tear, the application of a constant shear force results in an almost constant flow speed.

In the case of a three-dimensional cross-linking of the polymer chain, on the other hand, the viscous proportion is almost entirely lost, and only an elastic deformation can occur. An increase of the shear force finally leads to a mechanical tearing apart of the polymer structure up to a tearing apart of the entire film.

Thus, cross-linked and uncross-linked pressure-sensitive adhesive films show very different characteristics regarding their behavior upon shearing.

To examine this behavior, round cut-outs with a diameter of 12 mm were removed from the produced pressure-sensitive adhesive films. These round pieces of film were fixed between two strips of a polyethylene terephthalate film (Hostaphan RN 100, produced by Hoechst) as shown in Fig. 3.

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After clamping this arrangement into a commercial tensile testing machine (universal testing machine 81803, produced by Frank, Weinheim), the shear force per time which was necessary to achieve a constant shear speed of 2.5 mm/min was measured.

The thus obtained force/time diagrams of 6 individual measurements each are shown in Figs. 4 to 7.

In the case of the polyacrylate serving as reference, in the uncross-linked state a constant shear force is established after a short time which must be applied to maintain the predetermined constant shear speed: the polymer flows (Fig. 4).

In the cross-linked state, on the other hand, the shear force rapidly increases under elastic deformation until finally, the elastic expandability of the film is exceeded and the film tears, whereby the shear force rapidly drops off towards zero (Fig. 5).

The silicon film without a cross-linking additive shows a behavior very similar to that of the uncross-linked polyacrylate film: here, too, under a certain shear force the predetermined shear speed is maintained under flowing. The necessary forces are simply situated at a higher level, and the "energy barrier" for transition from the state of rest to a flowing movement is more distinct than with the uncross-linked polyacrylate (Fig. 6). This could be related to the different chain lengths and different intermolecular interaction forces of both polymer types.

What is decisive, however, is the characteristic change of the course in a cross-linker-containing silicone film. Very similarly to the cross-linked polyacrylate, a shear force is established under elastic deformation which finally drops off towards zero upon tearing of the film (Fig. 7).

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This is evident proof that the silicone pressure-sensitive adhesive film is no longer flowable after addition of the cross-linker titanyl acetylacetonate.

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CLAIMS

1. Process for the production of polysiloxane pressure-sensitive adhesive layers with reduced cold flow by means of coating and drying a one-component polysiloxane pressure-sensitive adhesive solution onto a suitable flat-shaped carrier, characterized in that a complex of a metal ion of the group consisting of calcium, magnesium, zinc, aluminum, titanium, zirconium or hafnium with a low-molecular organic complex former is added to the organic adhesive solution to be coated, whereby the metal ion is only released from the bond to the complex former under the conditions of heating and/or drying of the adhesive solution.
2. Process according to claim 1, characterized in that the metal additive amounts to at least 0.005 wt-%, relative to the dried adhesive mass.
3. Process according to claim 1, characterized in that the metal is provided in an amount of 0.005 to 0.5 wt-%, relative to the dried adhesive mass.
4. Process according to one or more of the preceding claims, characterized in that the organic complex former is substantially removed during drying.
5. Process according to one or more of the preceding claims, characterized in that the drying is carried out at a temperature of between 20 and 120°C.
6. Process according to one or more of the preceding claims, characterized in that the weight per unit area of the dried film is between 10 and 300 g/m².
7. Process according to one or more of the preceding claims, characterized in that the organic complex for-

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mer is acetylacetone or that acetylacetone participates in the complex forming.

8. Process according to one or more of the preceding claims, characterized in that the metal participating in the complex is aluminum or titanium.
9. Process according to one or more of the preceding claims, characterized in that the polysiloxane is substantially polydimethyl siloxane.
10. Process according to claim 9, characterized in that the free silanol groups present in the polydimethyl siloxane are chemically deactivated through a suitable end-capping and are thus amine-resistant.
11. Medicinal patch, characterized in that in its layered structure it has at least one layer of a polysiloxane pressure-sensitive adhesive produced by means of a process according to one of the preceding claims.

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ABSTRACT

In a process for the production of polysiloxane pressure-sensitive adhesive layers with reduced cold flow by means of coating and drying a one-component polysiloxane pressure-sensitive adhesive solution onto a suitable flat-shaped carrier, a complex of a metal ion of the group consisting of calcium, magnesium, zinc, aluminum, titanium, zirconium or hafnium with a low-molecular organic complex former is added to the organic adhesive solution to be coated, whereby the metal ion is only released from the bond to the complex former under the conditions of heating and/or drying of the adhesive solution.

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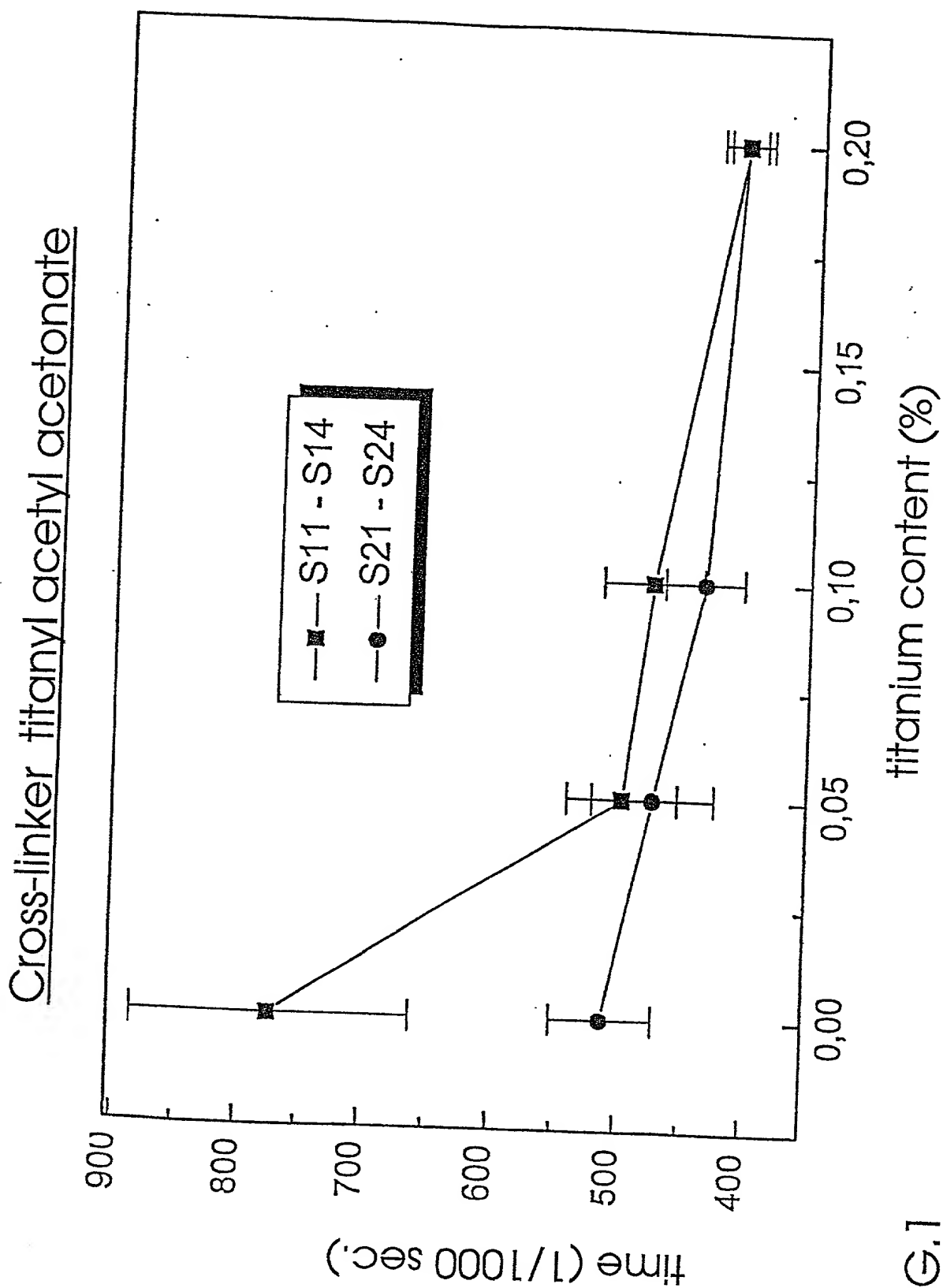


FIG.1

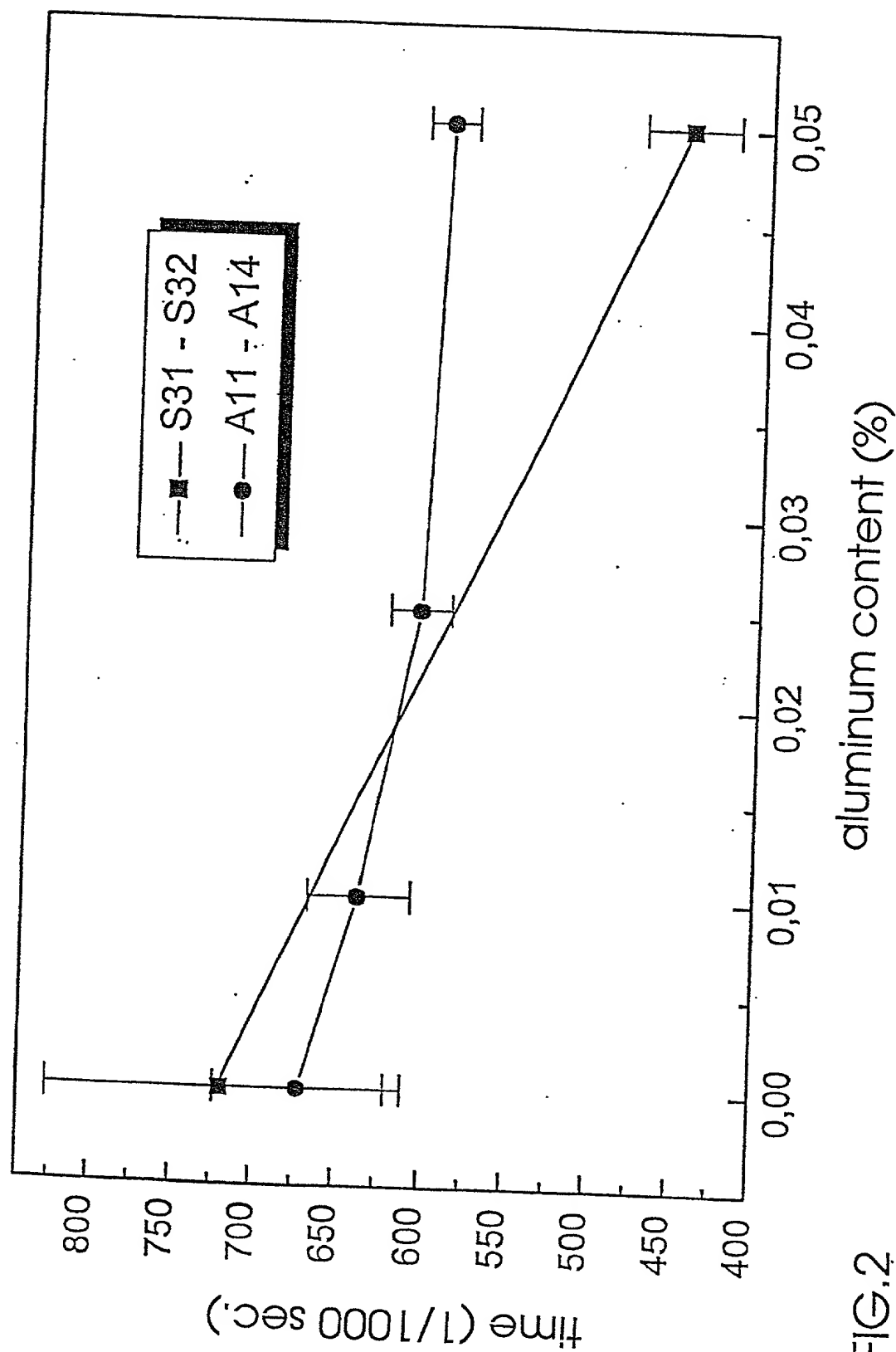
Cross-linker aluminum acetyl acetate

FIG.2

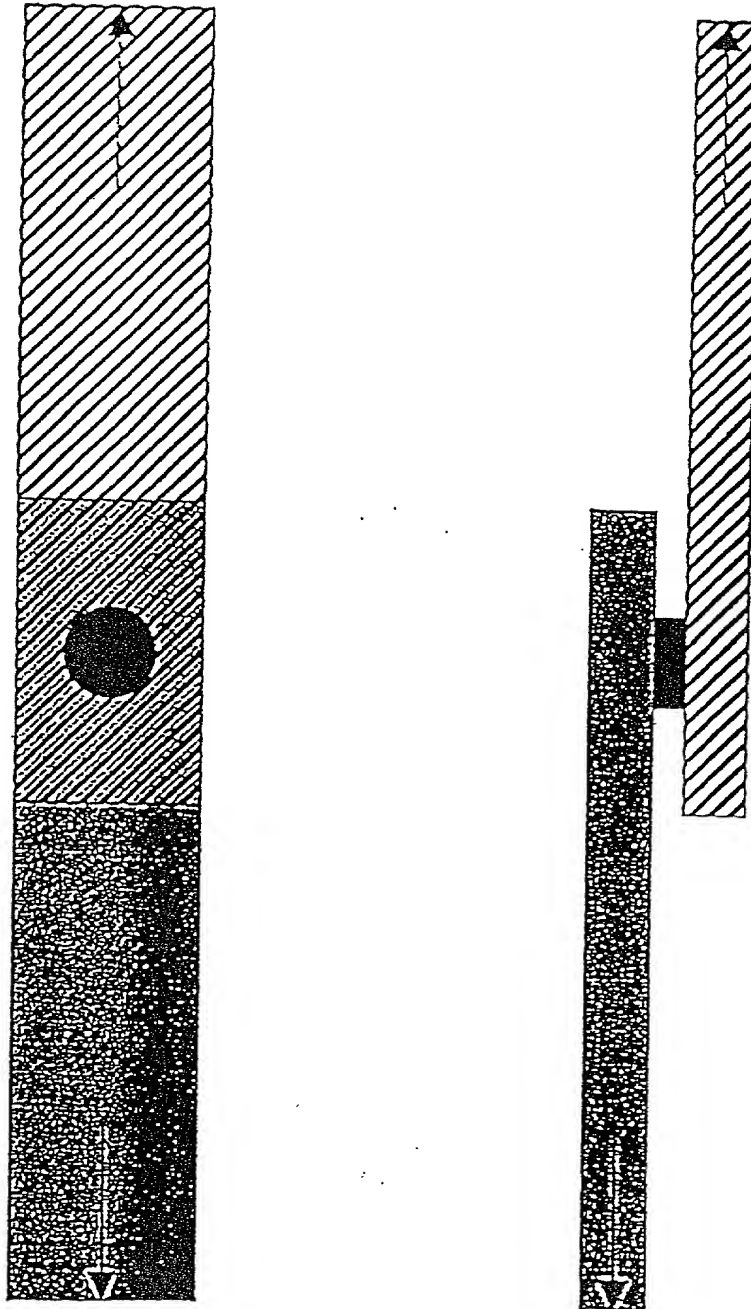


FIG.3

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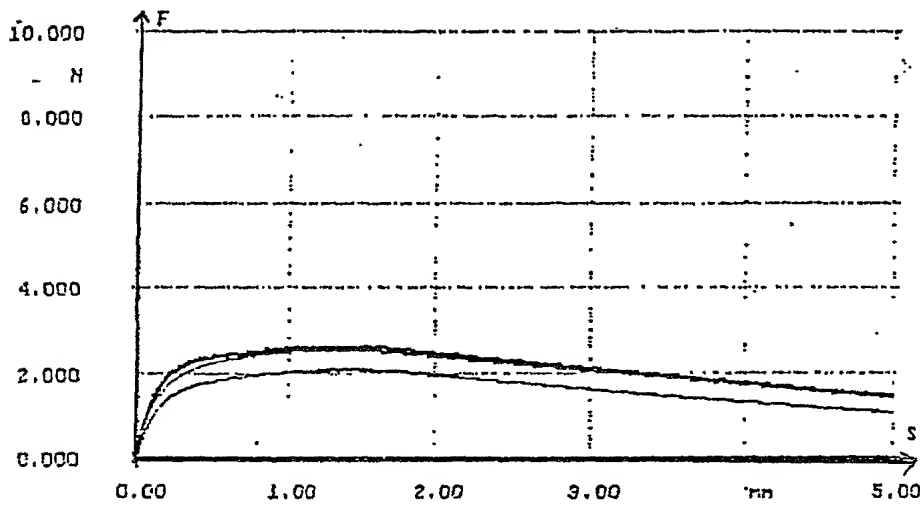


FIG.4

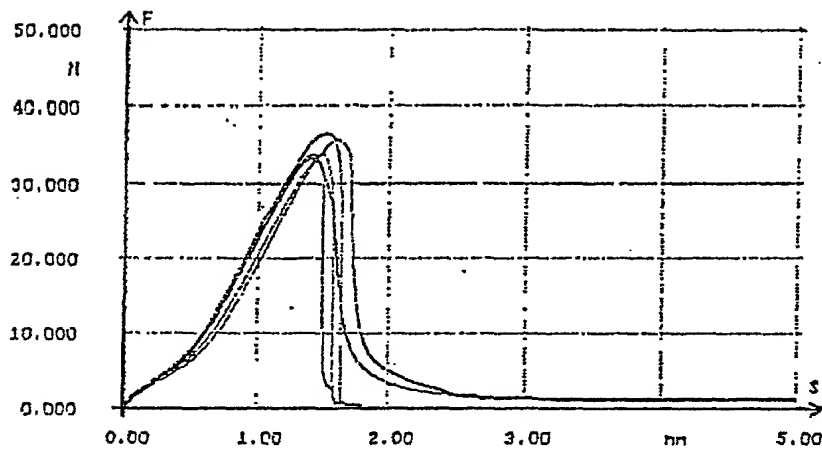


FIG.5

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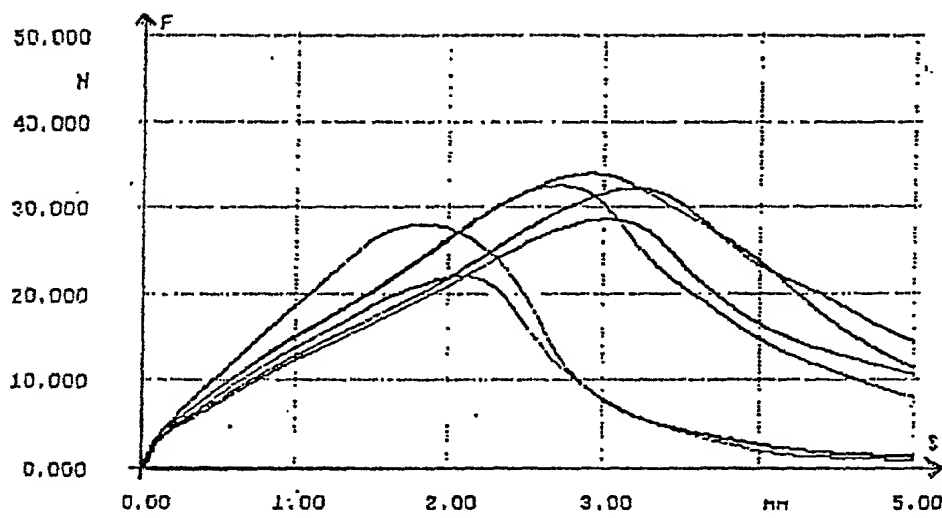


FIG.6

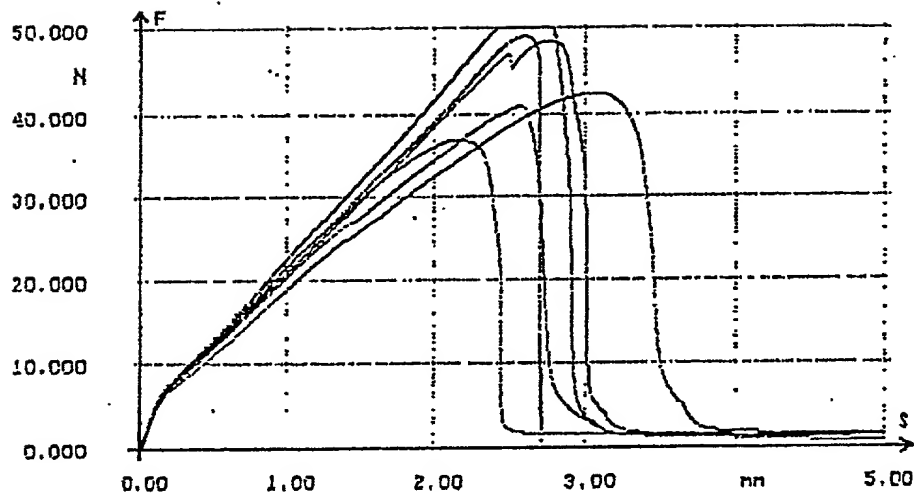


FIG.7

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Attorney Docket No. **RO0099US (#90568)**

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL,
DIVISIONAL, CONTINUATION OR CIP)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type: (check one applicable item below)

- ☐ original
☐ design

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application do not check any of next two items and check appropriate one of last three items.

- ☒ national stage of PCT
☐ supplemental

NOTE: If one of the following 3 items apply then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR CIP.

- ☐ divisional
☐ continuation
☐ continuation-in-part (CIP)

INVENTORSHIP IDENTIFICATION

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

SILICONE CONTACT ADHESIVE WITH REDUCED COLD FLOW

SPECIFICATION IDENTIFICATION

the specification of which: (complete (a), (b), or (c))

- (a) ☐ is attached hereto
(b) ☒ was filed on {**Express Mail Date: 12/15/2000**} as ☒ Serial No. **09/719,731** or
☐ Express Mail No. _____, as Serial No. not yet known
and was amended on _____ (if applicable); **and (c) below;**

- (c) (X) was described and claimed in PCT International Application No. **PCT/EP99/01246** filed on **February 26, 1999** and as amended under PCT Article 19 on (if any).

ACKNOWLEDGEMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations. Sec. 1.56(a).

- () In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.97.

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) () no such applications have been filed.
(e) (X) such applications have been filed as follows

NOTE: Where item (c) is entered above and the International Application which designated the U.S. claimed priority check item (e), enter the details below and make the priority claim.

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

COUNTRY	APPLICATION NO.	DATE OF FILING (month.day.year)	PRIORITY CLAIMED UNDER 37 USC 119
			() YES NO ()
			() YES NO ()
			() YES NO ()

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

German Appln. 198 11 218.1 filed March 14, 1998

and

PCT Appln. PCT/EP99/01246 filed February 26, 1999

POWER OF ATTORNEY

3 As a named inventor, I hereby appoint D. Peter Hochberg, Reg. No. 24,603, Katherine R. Vieyra, Reg. No. 47,155, and William H. Holt, Reg. No. 20,766, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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DIRECT TELEPHONE CALLS TO:
(Name and telephone number)

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1940 East 6th Street - 6TH Floor
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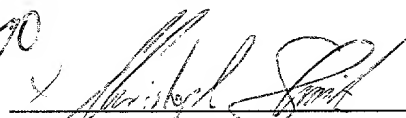
D. Peter Hochberg
(216) 771-3800

DECLARATION

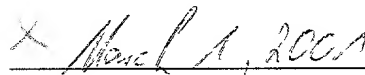
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

Full name of sole or first inventor: Christoph Schmitz

00
/ 

Inventor's signature



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